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# Degradation of diclofenac by pyrite catalyzed Fenton oxidation

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ABSTRACT

We demonstrated that diclofenac can be rapidly and completely oxidized in Fenton reaction system using pyrite as catalyst. The pH of the solution dropped from 5.7 to 4.1–3.2 with addition of different amounts of pyrite (0.5–4.0 mM) as Fe(II) concentration increased to 0.07–0.52 mM. Complete degradation (100%) of diclofenac was observed by pyrite Fenton system within 120 s, while only 65% of diclofenac was removed by classic Fenton system in 180 s. Degradation of diclofenac was significantly inhibited (100–51%) by addition of $HO^{\bullet}$ scavenger (*t*-butanol) but not by $O_2^{\bullet-}$ scavenger (chloroform), indicating that diclofenac was dominantly oxidized by $HO^{\bullet}$ produced during pyrite Fenton reaction. It was suggested that continuous dissolution of aqueous Fe(II) by pyrite Fenton reaction supported the complete degradation of diclofenac. The rate of diclofenac degradation increased as pyrite and $H_2O_2$ concentrations increased. 2,6-dichlorophenol, 2-chloroaniline, and 2-chlorophenol were detected as major intermediates but they were rapidly degraded in 120 s. Chloride ions, ammonium, and total organic carbon measurements confirmed that diclofenac finally degraded to further oxidized forms (organic acids, HCl, and $CO_2$).



## 1. Introduction

It has been reported that the trace level of pharmaceuticals is present in natural environments and wastewater [1–5] due to significant increase of usage [6,7]. Due to persistence of pharmaceuticals to human metabolism processes [8], they can be excreted through urine or feces. Then they enter municipal sewage treatment plants (STPs). Diclofenac (2-[(2, 6-dichlorophenyl)amino]phenylacetic acid), a non-steroidal anti-inflammatory drugs (NSAIDs), is one of the most frequently detected pharmaceuticals in STPs and surface waters [2,5,6]. It was not completely removed during wastewater treatment processes (only about 20–30% of removal efficiency) and thus entered the surface waters such as river and lake through STP-discharges [9,10]. Although it has been known that diclofenac can be rapidly degraded by photolysis in natural environments [2,11], still relatively high concentrations of diclofenac were detected in STPs-effluent and surface water (4.7 and 1.2 $\mu g\,L^{-1}$, respectively) [6,12]. This levels of diclofenac concentration can be a threat to aquatic living life such as rainbow trout (lowest observed effect concentration (LOEC): 5 $\mu g\,L^{-1}$ and no observed effect concentration (NOEC): 1 $\mu g\,L^{-1}$) [13]. Cleuvers and his coworkers demonstrated that the mixture of low concentration of NSAIDs (i.e., diclofenac, ibuprofen, naproxen, and acetylsalicylic acid) increased toxicity to *Daphnia* via cocktail effect [14].

Extensive efforts have been made to develop novel and effective treatment processes for the removal of diclofenac in natural and engineered environments. Especially, advanced oxidation processes (AOPs) producing reactive oxidant (hydroxyl radical ($HO^{\bullet}$): $E_0 = 2.76$ V) [15] have been studied as one of the promising technologies because of its success to remove diverse classes of pollutants. For example, oxidative degradation of diclofenac by $O_3$ [16], $O_3/H_2O_2$ [17], $UV/H_2O_2$ [18], photo-Fenton processes [19,20], and sonolysis [21] have been studied. However, these advanced treatment techniques except photo-Fenton processes are usually suffered from high operational costs and relatively slow removal kinetics [22]. Moreover, several toxic byproducts such as diclofenac-2,5-iminoquinone and 5-hydroxydiclofenac can be produced via ozone-based processes [16].

To overcome previously mentioned limitations of AOPs, cost effective and reactive catalysts such as (1) mixture of copper and manganese oxides, (2) mixture of nickel, copper, and iron, (3) aluminum oxide, (4) titanium dioxide, and (5) carbon nanotube have been introduced to oxidatively degrade diclofenac as heterogeneous catalytic materials [8,23]. These heterogenous catalysts did not form the toxic byproducts as ozone-based processes did, but degradation kinetics were relatively slow (i.e., the catalysts of 10 $g\,L^{-1}$ can degrade diclofenac of 20 $mg\,L^{-1}$ in 20–100 min) [8]. The photo-Fenton processes by titanium dioxide and carbon nanotube have shown the rapid degradation kinetics (i.e., the catalysts of 1 $g\,L^{-1}$ can degrade diclofenac of 8 $mg\,L^{-1}$ in 10 min) with

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generation of various byproducts during the reaction [23]. Therefore, novel and reactive catalyst should be introduced for rapid and complete degradation of diclofenac without producing toxic products.

Pyrite ($Fe^{II}S_2$), one of the most abundant iron sulfide minerals found in the earth's crust [24], can be a promising candidate for diclofenac removal. Pyrite has been successfully used as Fenton material for the oxidative degradation of organic contaminants such as trichloroethylene (TCE) and carbon tetrachloride (CT) [25,26]. The degradations of TCE and CT were significantly enhanced (removal efficiency: 97 and 93%, respectively) by heterogeneous Fenton reaction using pyrite and $H_2O_2$ (pyrite Fenton system) compared to that by homogenous Fenton reaction using aqueous Fe(II) (classic Fenton system) (removal efficiency: 77% and 52%, respectively) [25,26]. These results have shown that pyrite can be a potential and promising material to treat a variety of organic contaminants in STPs.

Although pyrite Fenton system have shown great potential to remove diclofenac, limited knowledge has been provided to understand the mechanism of diclofenac degradation. To date, the reactivity of pyrite has not been explored in heterogenous catalysis of diclofenac chemical oxidation. This is the first study investigating the degradation of diclofenac through Fenton oxidation catalyzed by pyrite. The main objectives of this study were to investigate the reactivity of pyrite to catalyze Fenton oxidation for diclofenac removal, to evaluate the influence of initial pyrite and $H_2O_2$ concentrations using central composite design (CCD) coupled with response surface methodology (RSM), to identify the major transformation products and its degradation mechanism.

## 2. Experimental

### 2.1. Materials

Diclofenac sodium salt ($C_{14}H_{10}Cl_2NNaO_2$), 2,6-dichlorophenol (99%), 2-chloroaniline (>99%), 2-chlorophenol (99%), and ferrous sulfate hepta-hydrate (99%) were purchased from Sigma-Aldrich. Hydrogen peroxide (30 wt.%) and titanium sulfate (24 wt.%) were purchased from Kanto. Tert-butanol (*t*-butanol) (>99%, Sigma) and chloroform (CF) (99.9%, Sigma) were used as hydroxyl radical ($HO^{\bullet}$) and superoxide radical ($O_2^{\bullet-}$) scavengers, respectively. Ethanol (95%, Jin chemical) and nitric acid (60%, DC chemical) were used for pyrite washing. Distilled water was purified by ultrapure filtration system (ELGA PURELAB Classic system) to obtain 18 MΩ cm pure deionized water (DIW). Pyrite (Zacatecas, Mexico) purchased from Ward's natural science was milled by ceramic mortar and pestle, and sieved (<150 μm) [27]. To remove fine particles and oxidized surface, sieved pyrite was ultra-sonicated in ethanol for 5 min and washed with 1 M nitric acid. Finally, pyrite was rinsed with deionized water and dehydrated with ethanol. Then it was dried and stored in a closed glass vial. Scanning electron microscope (SEM) image of pyrite exhibited non-uniformed shape of nano-sized particles (approximately 0.4–1.2 μm) (Fig. 1(a)). X-ray diffraction image of pyrite showed a good agreement with that in Joint Committee on Powder Diffraction Standards (JCPDS) diffraction data files (JADE 9, Materials Data Inc.) (Fig. 1(b)).

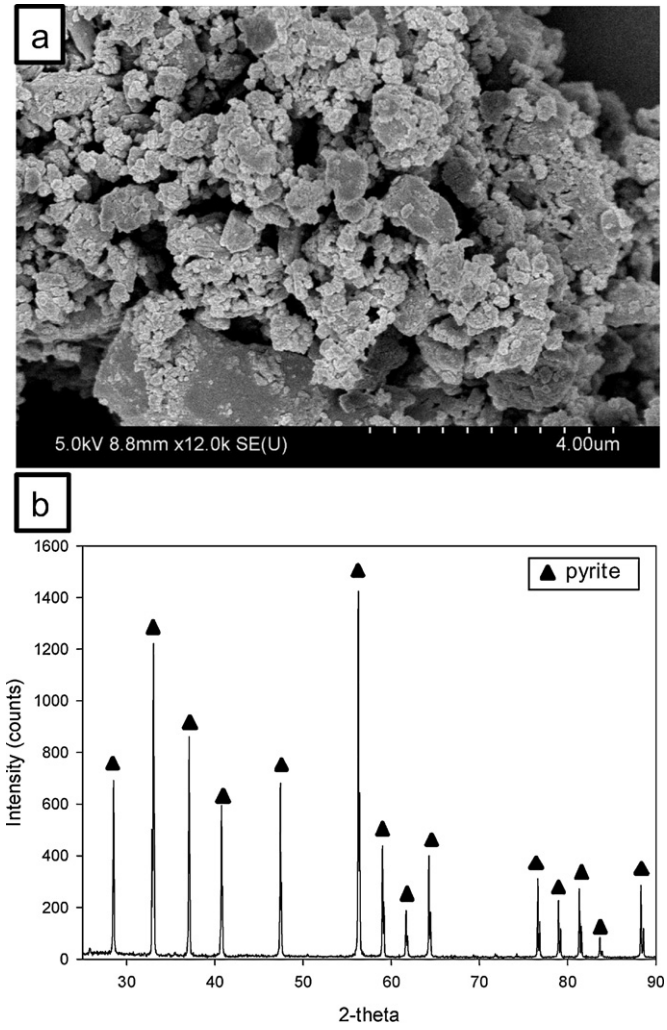


**Fig. 1.** SEM and XRD images of pyrite.

### 2.2. Precipitation of diclofenac in pyrite suspension

The experiments to investigate the pH drop in pyrite suspensions and diclofenac precipitation at pH 3 solution were carried out in a 200 mL glass flask equipped with a magnetic stirrer under aerobic conditions (oxygen: 21%) at room temperature (25 ± 0.5 °C). Unless stated otherwise, all experiments were conducted in ambient conditions. Exact amounts of pyrite (0.5–4.0 mM equivalent) were transferred to the glass flask containing 99.9 mL of DIW. The pH drop in pyrite suspensions was measured by pH meter (Thermo Orion, model 9272) equipped with an Orion Ross combination electrode. Aqueous Fe(II) concentration dissolved from pyrite surface was measured after the dissolution of pyrite was stopped to equilibrium. After pH was stabilized, an exact amount of $H_2O_2$ (100 μL, 1 M) was added to the glass flask to investigate further pH drop by addition of $H_2O_2$.

The precipitation of diclofenac at pH 3 was also investigated to choose initial concentration of diclofenac in this study. An exact amount (0.5 mL) of diclofenac stock solution prepared in DIW (10 g $L^{-1}$) was spiked to the glass flask containing pH 3 solution (99.4 mL) to make the initial concentration of 0.17 mM.

### 2.3. Degradation of diclofenac by pyrite suspension and $FeSO_4$ solution with $H_2O_2$

The experiments were conducted to characterize the degradation of diclofenac by pyrite Fenton system. Pyrite (0.006 g) was transferred to the glass flask containing 99.4 mL of DIW (0.06 g $L^{-1}$), which is equivalent to 0.5 mM of Fe(II). An exact amount (0.5 mL) of diclofenac stock solution prepared in DIW (1 g $L^{-1}$) was spiked to the glass flask (initial concentration: 0.017 mM) and degradation of diclofenac was initiated by adding 100 μL $H_2O_2$ (1 M) to prepare the initial $H_2O_2$ concentration of 1.0 mM. Unless stated otherwise,

**Table 1**
Variable levels of CCD for oxidative degradation of diclofenac by pyrite Fenton system.

| Process variables | Symbol | Actual values of the coded variable levels | | | | |
|---|---|---|---|---|---|---|
| | | −2 | −1 | 0 | 1 | 2 |
| Pyrite (mM) | $X_1$ | 0.42 | 1.27 | 3.33 | 5.39 | 6.24 |
| $H_2O_2$ (mM) | $X_2$ | 0.12 | 0.45 | 1.26 | 2.07 | 2.40 |

all experiments were conducted with the initial diclofenac concentration of 0.017 mM. Degradation of diclofenac was monitored by measuring concentration of diclofenac at each sampling time. Five controls (diclofenac + DIW, diclofenac + DIW + pyrite, diclofenac + DIW + $H_2O_2$, diclofenac + DIW + *t*-butanol, and diclofenac in pH 3 solution) were prepared to evaluate possible losses of diclofenac by sorption on wall of glass flask and pyrite surface, oxidation by $H_2O_2$, reaction with *t*-butanol, and precipitation at acidic pH, respectively. Degradation of diclofenac by classic Fenton system was tested using 0.5 mM of $FeSO_4$ at pH 4 solution, which were same Fe(II) concentration and initial pH with pyrite Fenton system. All samples and controls in this research were prepared in duplicate except the experiment for transformation products of diclofenac.

### 2.4. Degradation mechanism studies

To investigate the mechanism of diclofenac degradation by pyrite Fenton system, several experiments were conducted. To identify the main reactant between $HO^{\bullet}$ and $O_2^{\bullet-}$ in pyrite Fenton system, appropriate amounts (10:1, 50:1, and 100:1 molar ratios of scavengers (*t*-butanol and CF) to diclofenac) of each scavenger were added to the solutions prior to the addition of $H_2O_2$. The pyrite Fenton reaction was initiated by addition of pyrite (0.5 mM) and $H_2O_2$ (1.0 mM).

The concentration of aqueous Fe(II) and Fe(III), and $H_2O_2$ at each sampling time were measured. The experiments were prepared by following the procedure described below.

The oxidative degradations of diclofenac by homogenous and heterogenous Fenton reactions were compared to evaluate the contribution of each reaction on the degradation kinetics of diclofenac. For the preparation of homogenous Fenton reaction, pyrite (0.006 g) was transferred to the glass flask containing 99.4 mL of DIW and equilibrium time (3 min) was given for full dissolution of aqueous Fe(II) from pyrite surface into the suspension. The suspension was centrifuged at 12,000 rpm for 2 min, then aliquot was filtered with 0.2-μm sterilized PTFE membrane filter (Whatman) to remove pyrite solid. The diclofenac stock solution was spiked to the glass flask (initial concentration: 0.017 mM) and 1.0 mM $H_2O_2$ was added to initiate the homogenous Fenton reaction for degradation of diclofenac. The experimental data for heterogenous Fenton reaction was obtained from the experiment previously conducted.

### 2.5. Effect of pyrite and $H_2O_2$ concentrations on kinetics of diclofenac degradation

The effect of environmental factors was tested using CCD and RSM. CCD with two factors (i.e., varying initial concentrations of pyrite and $H_2O_2$) and five coded levels were used to design each experimental condition. All kinetic experiments were conducted at same experimental condition suggested by CCD except that the concentrations of pyrite (0.42–6.24 mM) and $H_2O_2$ (0.12–2.40 mM) were changed. The detailed experimental ranges and coded variable levels tested in each CCD were listed in Table 1. The variables $X_i$ were coded as $x_i$ based on the following equation:

$$x_i = \frac{X_i - X_{i,o}}{\delta X_i}, (i = 1 \text{ and } 2) \quad (1)$$

where $X_i$ is the real value of the independent variable, $X_{i,0}$ is the value of $X_i$ at the center point of the investigated area and the $\delta X_i$ is the step change. The concentration of pyrite ($X_1$) and $H_2O_2$ ($X_2$) was chosen as the independent input variables. The degradation rate constant of diclofenac was used as the dependent output variable. The quadratic polynomial model was used to fit the response variable as following equation:

$$Y = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j \quad (2)$$

where *Y* is the degradation kinetic of diclofenac (pseudo-first order, $s^{-1}$), $b_0$ is the offset term known as a constant, $b_i$ are the linear coefficients, $b_{ii}$ are the quadratic coefficients, $b_{ij}$ are the interaction coefficients, and $x_i$ and $x_j$ are the coded values of the independent input variables.

### 2.6. Analytical methods

The concentrations of diclofenac, 2,6-dichlorophenol, 2-chloroaniline, and 2-chlorophenol in aqueous solution was measured by high performance liquid chromatography (HPLC) (Varian ProStar) equipped with a C18 packed column (Shiseido) and UV detector. 0.9 mL of sample was collected at each sampling time. Then the aliquot was immediately transferred to 1.5 mL conical tubes containing 0.1 mL of 1 M *t*-butanol (100 mM) and vortexed to scavenge $HO^{\bullet}$. The tubes were centrifuged at 12,000 rpm for 2 min and 0.8 mL of supernatant was transferred to each HPLC auto-sampler vial (2 mL). Mobile phase of this analysis was a mixture of 30% DIW (containing 0.01% $CH_3COOH$) and 70% acetonitrile. The target and products were measured at a flow rate of 1.0 mL $min^{-1}$ at a wave length of 240 nm for 8 min.

To observe the morphology of pyrite surfaces, SEM analysis was conducted by FE type SEM (SEM, S4800 model, Hitachi). The preparation procedure was followed as previously reported [28]. XRD analysis was conducted to identify the purity of pyrite used in this study using Rigaku automated diffractometer with Cu KN radiation (D/MAX-2500). The scan range was 20 to 90° 2$\theta$ with a scan speed of 1° $min^{-1}$.

Aqueous Fe(II), Fe(III), and $H_2O_2$ concentrations in solution were measured using a UV/visible spectrophotometer (Agilent 8453). Samples were quenched with *t*-butanol to stop the further degradation of diclofenac by residual hydroxyl radical and filtered with 0.2 μm membrane filter. The concentration of aqueous Fe(II) and total aqueous Fe was measured by using ferrozine method [29,30]. Total aqueous Fe concentration was also measured by adding a 10% hydroxylamine solution [31]. Aqueous Fe(III) concentration was calculated by subtracting aqueous Fe(II) concentration from total aqueous Fe concentration. $H_2O_2$ concentration was measured at 405 nm using titanium sulfate method [32].

Chloride ions released from the degradation of diclofenac was analyzed by ion chromatography (IC, Metrohm 881 Compact) with Metrosep A Supp 5 150 column (4 mm × 150 mm) and conductivity detector. Eluent was made of a binary mixture of 3.2 mM $Na_2CO_3$ and 1.0 mM $NaHCO_3$ and its flow rate was constant at 0.7 mL $min^{-1}$. Ammonium concentration was analyzed by IC with Metrosep C 4 150 column (4 mm × 150 mm). Eluent was made of a binary mixture of 1.7 mM $NHO_3$ and 0.7 mM pyridine-2, 6-dicarboxylic acid and its flow rate was constant at 1.0 mL $min^{-1}$. Total organic carbon (TOC) was measured using a Pheonix 8000 TOC analyzer (Tekmar-Dohrmann) operated in TOC mode.

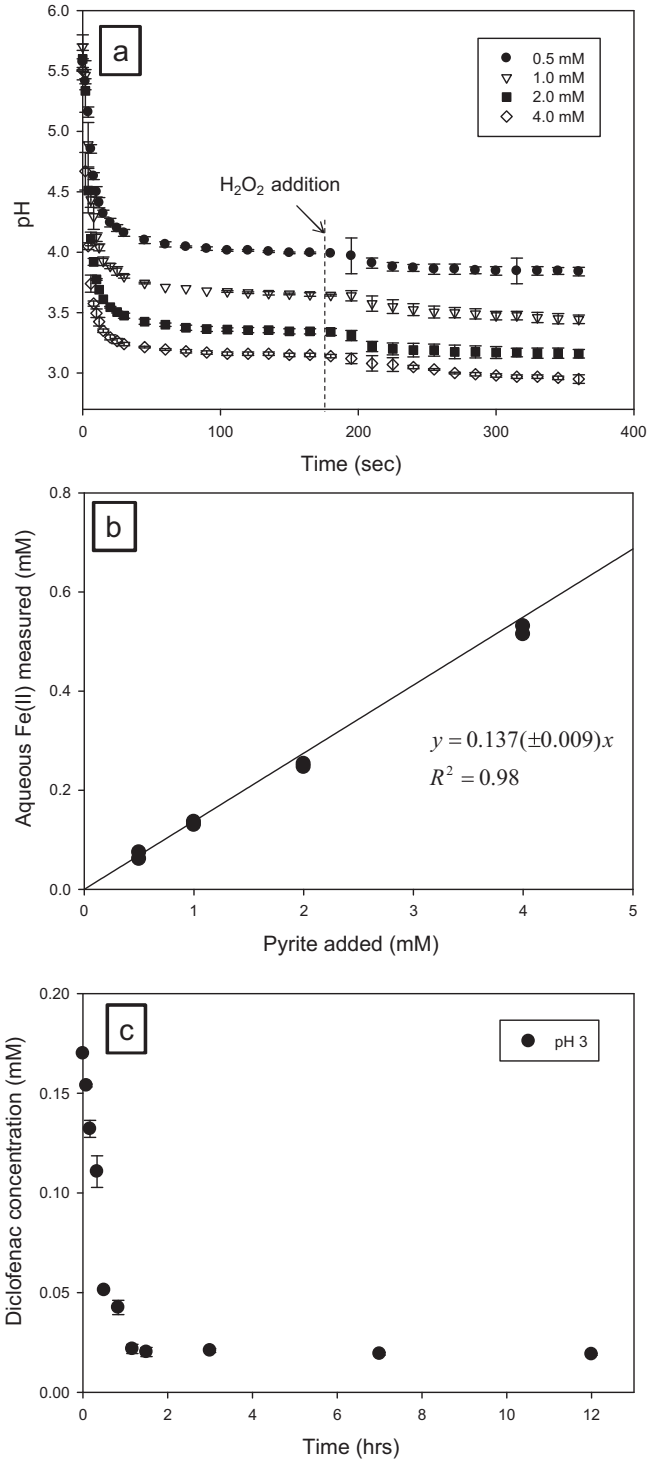


**Fig. 2.** (a) pH drop by addition of pyrite and $H_2O_2$. (b) Increase of aqueous Fe(II) concentration with respect to increase of pyrite loading in suspensions. Experimental boundary conditions: $[Diclofenac]_0 = 0.017$ mM, $[pyrite]_0 = 0.5–4.0$ mM, $[H_2O_2]_0 = 1.0$ mM, and temperature = 25 ± 0.5 °C. (c) Precipitation of diclofenac in acidic suspension (pH 3).

## 3. Results and discussion

### 3.1. pH drop and increase of aqueous Fe(II) in pyrite suspension

Fig. 2(a) shows pH drop in pyrite suspension by subsequent additions of pyrite and $H_2O_2$. The pH dropped immediately from 5.7 to 4.1–3.2 by additions of different loading of pyrite (0.5–4.0 mM equivalent) within 50 s, then decreased more to pH 3.8–3.0 by addition of $H_2O_2$ (1.0 mM) in 6 min. This was due to rapid dissolution of Fe(II) from pyrite surface into the suspension at aerobic condition (20% oxygen at 25 °C) (Eq. (3)) and oxidation of pyrite by $H_2O_2$ (Eq. (4)), which can significantly increase $H^+$ in the suspension [33].

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4{}^{2-} + 4H^+ \quad (3)$$

$$2FeS_2 + 15H_2O_2 \rightarrow 2Fe^{3+} + 4SO_4{}^{2-} + 2H^+ + 14H_2O \quad (4)$$

Aqueous Fe(II) concentration released from pyrite was also measured. The aqueous Fe(II) concentration increased by 7.4 times (from 0.07 mM to 0.52 mM) as the loading of pyrite increased by 8 times (from 0.5 mM to 4.0 mM equivalent). The linear relationship between Fe(II) concentration and pyrite loading is shown in Fig. 2(b). A linear regression fit of Fig. 2(b) (slope: 0.137 ± 0.009) indicates that almost 14% molar equivalent Fe(II) are dissolved into the suspension from pyrite surface. It has been well known that the aqueous Fe(II) are required to produce $HO^\bullet$ with the presence of $H_2O_2$ (Eq. (5)) [33].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^\bullet \quad (5)$$

These results demonstrated that pyrite has a benefit as Fenton reaction media because pyrite provides both proper pH condition (normally pH 3–4) and aqueous Fe(II) concentration at the same time. Lower pH and constant Fe(II) concentration are required for the Fenton reaction. For the oxidative degradation of diclofenac, however, the pH drop induced by pyrite dissolution should be carefully considered because the solubility of diclofenac is strongly affected by pH condition due to low $pK_a$ value of 4.15 [34]. Indeed, simultaneous removal reactions (i.e., precipitation–redissolution–degradation) have been observed during the oxidative degradation of diclofenac by photo-Fenton reaction [20]. The maximum solubility of diclofenac at pH 3 was checked to avoid the influence of precipitation on the removal efficiency of diclofenac in this study. Fig. 2(c) shows the variation of diclofenac concentration in aqueous phase at pH 3 with respect to time. Initially, 0.170 mM of diclofenac was spiked to the solution and diclofenac concentration in aqueous phase was monitored. The concentration dropped to 0.020 mM in 1 h, then stayed at constant values (0.018–0.020 mM) for 12 h. Therefore, 0.017 mM of diclofenac was used as an initial concentration (5 mg $L^{-1}$) for all kinetic experiments. Although the initial concentration was much higher than those detected in STPs-effluent and surface water (4.7 and 1.2 μg $L^{-1}$) [6,12], we used the concentration due to the rapid degradation kinetics of diclofenac by pyrite Fenton reaction and detection limit of transformation products.

### 3.2. Degradation kinetics of diclofenac by pyrite catalyzed Fenton oxidation

Fig. 3 shows the degradation kinetics of diclofenac in pyrite and classic Fenton systems at pH 4. Control tests were conducted to check potential losses of diclofenac during the Fenton reaction. Recoveries from all control were more than 95% for 180 s, indicating there were no significant losses of diclofenac due to sorption on the glass flask and pyrite, reduction by pyrite surface, oxidation by $H_2O_2$, reaction with *t*-butanol, and precipitation at acidic pH (pH 3) during the time frame of pyrite and classic Fenton reactions. Complete degradation of diclofenac was observed in 120 s with pyrite Fenton system, while only 65% of diclofenac was removed by classic Fenton system in 180 s. This showed that pyrite Fenton reaction surpassed classic Fenton reaction in diclofenac degradation when they have same amount of Fe(II) in the system. The degradation kinetics of diclofenac in the pyrite Fenton system can be properly described by the pseudo-first-order kinetics (0.164 ± 0.032 $s^{-1}$,

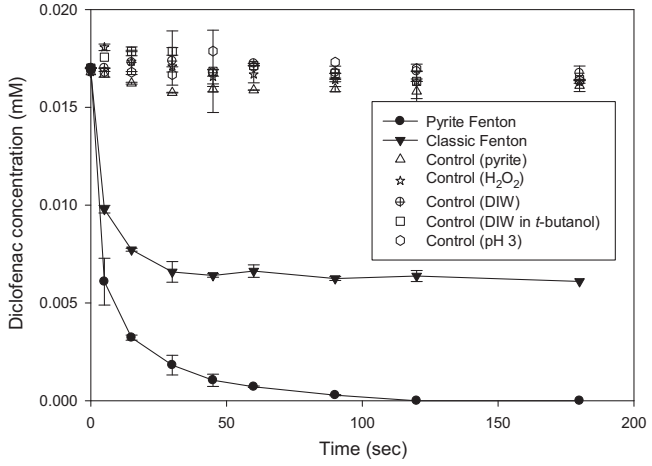


**Fig. 3.** Degradation kinetics of diclofenac under different experimental conditions (5 types of controls, classic Fenton reaction, and pyrite Fenton reaction). Experimental boundary conditions: $[Diclofenac]_0 = 0.017$ mM, $[pyrite]_0 = 0.5$ mM, $[H_2O_2]_0 = 1.0$ mM, initial pH 4.0, and temperature = 25 ± 0.5 °C.

$R^2 = 0.96$), while that in the classic Fenton system showed an early termination of diclofenac degradation.

To investigate the different degradation kinetics between pyrite and classic Fenton reactions, we measured the concentration profile of aqueous Fe(II) during the reactions (Fig. 4). As shown in Fig. 2, addition of 0.5 mM pyrite into the solution produced 0.080 mM of initial aqueous Fe(II) in pyrite Fenton system. Initial aqueous Fe(II) concentration decreased to 0.022 mM in 45 s after the pyrite Fenton reaction initiated, then slightly increased to 0.027 mM in 300 s. This indicated that low but enough concentration of aqueous Fe(II) for maintaining Fenton reaction can be continually dissolved from pyrite surface in pyrite Fenton system. Both Fe(II) (Eq. (3)) and HO• (Eq. (5)) generating reactions can be major rate limiting steps depending on $H_2O_2$ concentration in the pyrite Fenton system, while its rate limiting step in classic Fenton system is only HO• generating reaction [15,35]. Therefore, the generation of Fe(II) from pyrite surface into the suspension can be a rate limiting step when sufficient amount of $H_2O_2$ (1.0 mM) was added in the pyrite Fenton system resulting in the pseudo-first-order kinetics [25]. Compared to the pyrite Fenton system, the initial aqueous Fe(II) concentration (0.5 mM) in classic Fenton system dramatically decreased to 0.045 mM in 90 s and even highly decreased to 0.010 mM in 300 s. The aqueous Fe(II) concentration in classic Fenton system was higher than that in pyrite Fenton system until 90 s, and became lower after 120 s. In classic Fenton system, Fe(II) was mostly in aqueous phase and its concentration was much higher than that in pyrite Fenton system, easily leading to a scavenging reaction with HO• (Eq. (6), $k_{HO^\bullet, Fe^{2+}} = 5 \times 10^8\ M^{-1}\ s^{-1}$) [36]. This may significantly inhibit the diclofenac degradation in the classic Fenton system in 90 s.

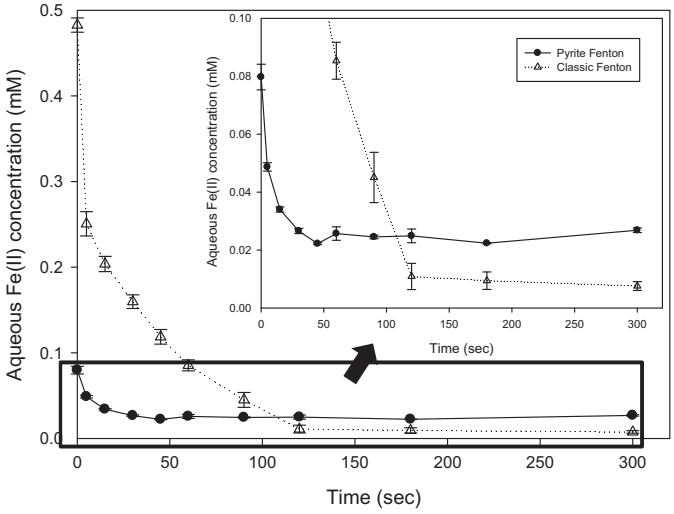


**Fig. 4.** Concentrations of aqueous Fe(II) in pyrite and classic Fenton systems during the degradation of diclofenac. Experimental boundary conditions: $[Diclofenac]_0 = 0.017$ mM, $[pyrite]_0 = 0.5$ mM, $[FeSO_4]_0 = 0.5$ mM, $[H_2O_2]_0 = 1.0$ mM, initial pH 4.0, and temperature = 25 ± 0.5 °C.

$$Fe^{2+} + HO^\bullet \rightarrow Fe^{3+} + OH^- \quad (6)$$

After 90 s, the degradation of diclofenac in the classic Fenton system seems to be ceased due to the total low aqueous Fe(II) concentration (≤0.01 mM) which can extremely decrease the production of HO• in the classic Fenton system. Indeed, we also observed the termination of reaction in homogenous Fenton reaction when the total aqueous Fe(II) concentration in the suspension reached ~0.01 mM (next section). The results showed a potential possibility that an excessive amount of initial aqueous Fe(II) and its early consumption can significantly inhibit the oxidative degradation of diclofenac in classic Fenton system.

### 3.3. Degradation mechanism of diclofenac by pyrite catalyzed Fenton oxidation

It has been known that $H_2O_2$ can mainly produce HO• but also other radicals such as $O_2^{\bullet-}$ and hydroperoxyl radical (OOH•) during the Fenton reaction [37,38]. Hydroperoxyl radical may not significantly affect the degradation kinetic of diclofenac due to lower oxidation potential and non-reactivity in aqueous system [38]. However, it has been widely reported that $O_2^{\bullet-}$ can reduce organic contaminants such as CT and Rhodamine B in other studies [26,39,40]. Diclofenac is also subject to reductive degradation, thus the role of $O_2^{\bullet-}$ must be considered. Experiments were conducted to investigate the role of $O_2^{\bullet-}$ and HO• on the degradation kinetics of diclofenac by pyrite Fenton system. Fig. 5 shows degradation kinetics of diclofenac in pyrite Fenton systems with and without CF or *t*-butanol. CF has been widely used as $O_2^{\bullet-}$ scavenger ($k_e = 3 \times 10^{10}\ M^{-1}\ s^{-1}$) [40], and *t*-butanol has been used as HO• scavenger [40,41]. There was no significant difference in the degradation kinetics of diclofenac with CF while varying molar ratios of CF to diclofenac from 10:1 to 100:1 (Fig. 5 (a)). The results indicate that reductive pathway by $O_2^{\bullet-}$ is not an important process in this study. In contrast to the addition of CF, addition of *t*-butanol significantly affected the degradation of diclofenac (Fig. 5 (b)). Diclofenac was completely degraded in the pyrite Fenton system without *t*-butanol, but was significantly inhibited by addition of *t*-butanol. The degradation efficiency was 83% after 180 s when a molar ratio of *t*-butanol to diclofenac was 10:1, and gradually decreased as its ratio increased to 50:1 (66%) and 100:1 (51%). Incomplete inhibition of diclofenac degradation by addition of *t*-butanol can be explained by comparing 2nd order rate constants of HO• with *t*-butanol and diclofenac. The 2nd order rate constant of HO• with diclofenac ($k_{HO^\bullet, diclofenac} = 7.5 \times 10^9\ M^{-1}\ s^{-1}$) [42] is 12.5 times greater than that with *t*-butanol ($k_{HO^\bullet, t\text{-butanol}} = 6 \times 10^8\ M^{-1}\ s^{-1}$) [43]. Thus *t*-butanol could not completely inhibit the reaction when 100 times higher molar ratio of *t*-butanol was added. However, no significant degradation was observed at 100 mM of *t*-butanol (our quenching method, data not shown) indicating that ratio of 5882:1 was high enough to quench the generated HO• during pyrite Fenton reaction. These results clearly showed that diclofenac was oxidatively degraded by HO• in pyrite Fenton system.

Fig. 6 shows concentration profiles of aqueous Fe(II), Fe(III), total Fe, and $H_2O_2$ during the course of diclofenac degradation by pyrite Fenton reaction. Aqueous Fe(II) concentration rapidly dropped in

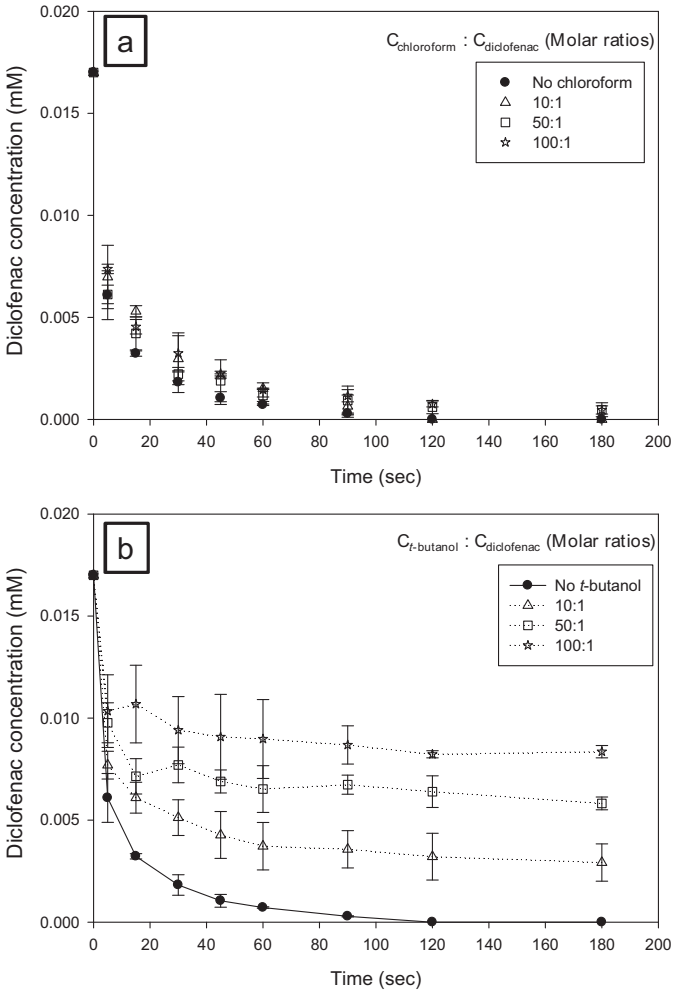


**Fig. 5.** Effect of (a) HO• scavenger (*t*-butanol) and (b) $O_2^{\bullet-}$scavenger (chloroform) on the degradation kinetics of diclofenac by pyrite Fenton reaction. Experimental boundary conditions: $[Diclofenac]_0 = 0.017$ mM, $[pyrite]_0 = 0.5$ mM, $[H_2O_2]_0 = 1.0$ mM, and temperature = 25 ± 0.5 °C.

45 s and slightly increased in 180 s as described above, while aqueous Fe(III) concentration was rapidly increased to 0.077 mM in 45 s and slowly increased to 0.087 mM in 180 s. The concentration of $H_2O_2$ was continuously decreased from 1 mM to 0.81 mM in 180 s. This indicated that limited amount of aqueous Fe(II) reacted with

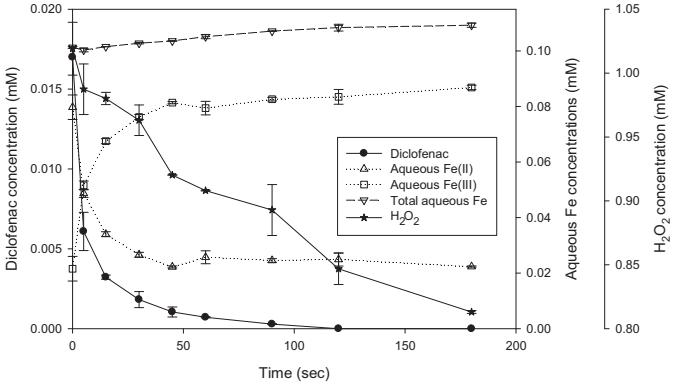


**Fig. 6.** The concentrations of diclofenac, aqueous Fe(II), Fe(III), total aqueous Fe, and $H_2O_2$ along with the catalytic oxidation of diclofenac by pyrite Fenton reaction. Experimental boundary conditions: $[Diclofenac]_0 = 0.017$ mM, $[pyrite]_0 = 0.5$ mM, $[H_2O_2]_0 = 1.0$ mM, and temperature = 25 ± 0.5 °C.

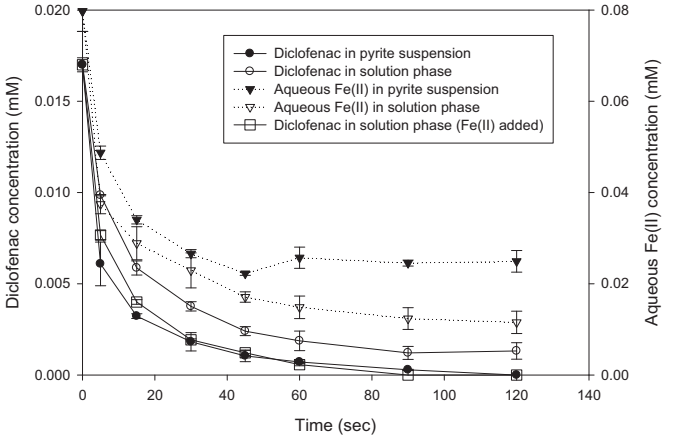


**Fig. 7.** Contributions of homogenous and heterogenous Fenton reactions on the degradation kinetics of diclofenac and consumptions of aqueous Fe(II) along with the catalytic oxidation of diclofenac by each reaction and additions of $FeSO_4$ solution during the degradation of diclofenac in homogenous Fenton reaction. Experimental boundary conditions: $[Diclofenac]_0 = 0.017$ mM, $[pyrite]_0 = 0.5$ mM, $[H_2O_2]_0 = 1.0$ mM, and temperature = 25 ± 0.5 °C.

sufficient amount of $H_2O_2$ resulting the accumulation of aqueous Fe(III) in the suspension. The ratio of the consumed $H_2O_2$ to the degraded diclofenac was 11:1, which indicated that generated HO• was efficiently reacted with diclofenac in pyrite Fenton system. Higher ratio of the value (1450:1) has been observed during the oxidative degradation of *p*-nitrophenol by magnetite Fenton system due to the production of non-radicals such as $O_2$ and $H_2O$ by 2 electron transfer reactions rather than generation of HO• [41]. The rapid degradation of diclofenac (in 120 s) in pyrite Fenton system, therefore, may be caused by the proper amount of HO• and its efficient use for diclofenac degradation.

Many studies have suggested that the decomposition of $H_2O_2$ can be controlled by surface-catalyzed process in the heterogenous reaction using iron oxides (e.g., magnetite, goethite, and hematite) under circumneutral pH conditions [44,45]. The complex between surface bound Fe(III) ($\equiv Fe^{3+}$) and $H_2O_2$ is formed with the addition of $H_2O_2$ in iron oxide suspension (Eq. (7)), then surface bound $H_2O_2$ reduces Fe(III) to Fe(II) and produces OOH• (Eq. (8)). The generated $\equiv Fe^{2+}$ may further react with $H_2O_2$ to produce HO• (Eq. (9)), which can react with target contaminants.

$$\equiv Fe^{3+} + H_2O_2 \rightarrow \equiv Fe^{3+}H_2O_2 \quad (7)$$

$$\equiv Fe^{3+}H_2O_2 \rightarrow \equiv Fe^{2+} + OOH^{\bullet} + H^{+} \quad (8)$$

$$\equiv Fe^{2+} + H_2O_2 \rightarrow \equiv Fe^{3+} + HO^{\bullet} + OH^{-} \quad (9)$$

To investigate the role of surface-catalyzed process in pyrite Fenton reaction during diclofenac degradation, two different kinetic experiments were compared. One is conducted with the same manner of pyrite Fenton reaction. In the other reaction, pyrite solids were removed before the addition of diclofenac to compare the effect of pyrite solids presence in suspension. Ninety percentage of diclofenac was degraded by the homogenous reaction (solution only phase) in 120 s compared to the complete degradation (100%) by heterogenous reaction (Fig. 7) indicating that most diclofenac in pyrite Fenton system was degraded by HO• produced from dissolved Fe(II) (Eq. (5)) not by surface-catalyzed process (Eq. (9)). This was due to the acidic pH leading to the decomposition of $H_2O_2$ by dissolved Fe species rather than surface Fe [46]. Remained diclofenac (10%) may be further degraded by continuous dissolution of aqueous Fe(II) in heterogenous reaction as described above. To support our hypothesis, the concentration of aqueous Fe(II) in homogenous reaction was monitored and compared with that of heterogenous reaction (Fig. 7). The initial

aqueous Fe(II) (0.080 mM) in the homogenous reaction continuously decreased to 0.01 mM in 120 s. All measured values were lower than those in the heterogenous reaction indicating that the amounts of produced Fe(II) from pyrite surface was equal to the differences between homogenous and heterogenous reactions. To verify the role of produced Fe(II) in heterogenous Fenton system, we gradually added an appropriate amount of aqueous Fe(II) (i.e., 0.0024 mM) at 2, 10, 20, 35, 50, 75, and 100 s (total: 0.017 mM) during homogenous Fenton system which was equal to the difference between homogenous and heterogenous reactions at 120 s (0.017 mM) (Fig. 7). The enhanced degradation of diclofenac was observed by addition of aqueous Fe(II) rather than that by homogenous Fenton reaction, but still lower than that of heterogenous Fenton reaction in 30 s because the amount of dissolved aqueous Fe(II) in heterogenous Fenton reaction (0.01 mM) was higher than the aqueous Fe(II) added until 30 s (0.007 mM). However, the degradation kinetic seems to be almost identical with heterogenous Fenton reaction after 30 s. These results confirmed that continuing dissolution of aqueous Fe(II) from pyrite surface was the key factor to completely degrade diclofenac in pyrite Fenton reaction.

### 3.4. Effect of pyrite and $H_2O_2$ concentrations on the degradation kinetic of diclofenac

A total of 10 experiments were conducted for RSM development to investigate the effect of pyrite and $H_2O_2$ loadings on the degradation kinetic of diclofenac in pyrite Fenton system (Table 2). An ANOVA analysis was carried out and the results for the coded variable levels are presented in Table 3. The model F-value of 51.81 implies that the model was meaningfully significant, and a value of 'Prob > $F$' less than 0.05 indicates that the model terms were significant at 95% confidence level. The results indicated that $X_1$, $X_2$, $X_1^2$, and $X_2^2$ were significant model terms for degradation rate constants in this study. Although term of $X_1X_2$ was insignificant ($P > 0.05$), it cannot be eliminated to support the hierarchy of the model due to the model correlation coefficient ($R^2 = 0.985$), suggesting a good agreement between the experimental and predicted values of the degradation rate constant of diclofenac. Eq. (10) shows the derived quadratic polynomial model obtained by using Eq. (2) which represents the relationship between degradation rate constant of diclofenac and the independent input variables.

$$Y = -1.04687 + 0.49760X_1 + 1.28265X_2 + 0.003813X_1X_2 - 0.052738X_1^2 - 0.026767X_2^2 \quad (10)$$

where $X_1$, $X_2$, and $Y$ are the concentrations of pyrite and $H_2O_2$ (mM), and rate constant ($s^{-1}$), respectively. Fig. 8 shows the strong linear correlation between experimental and predicted values of degradation rate constants. The results demonstrate that derived model is adequate to investigate the effect of both pyrite and $H_2O_2$ concentrations on degradation kinetic of diclofenac in pyrite Fenton system.

Fig. 9 shows the two-dimensional contour lines and three-dimensional response surfaces obtained by the results of degradation rate constant with variation of two variables (i.e., pyrite and $H_2O_2$). The optimum dosage for pyrite and $H_2O_2$ could not be obtained in this study because diclofenac degradation was completed in few seconds at high concentrations of pyrite and $H_2O_2$. Instead, the degradation rate constant gradually increased as concentrations of pyrite and $H_2O_2$ increased, and showed a saturation pattern after concentrations of pyrite and $H_2O_2$ over 4.36 and 1.66 mM, respectively. This indicated that once optimal amounts of pyrite and $H_2O_2$ were introduced to the pyrite Fenton system, further additions of them did not significantly affect the degradation kinetics of diclofenac. Increase of pyrite

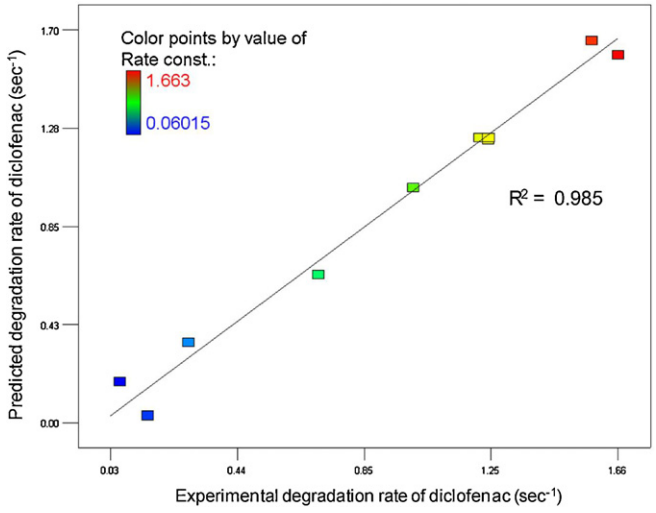


**Fig. 8.** Comparison of diclofenac degradation rates obtained by the experiment values and model predicted.

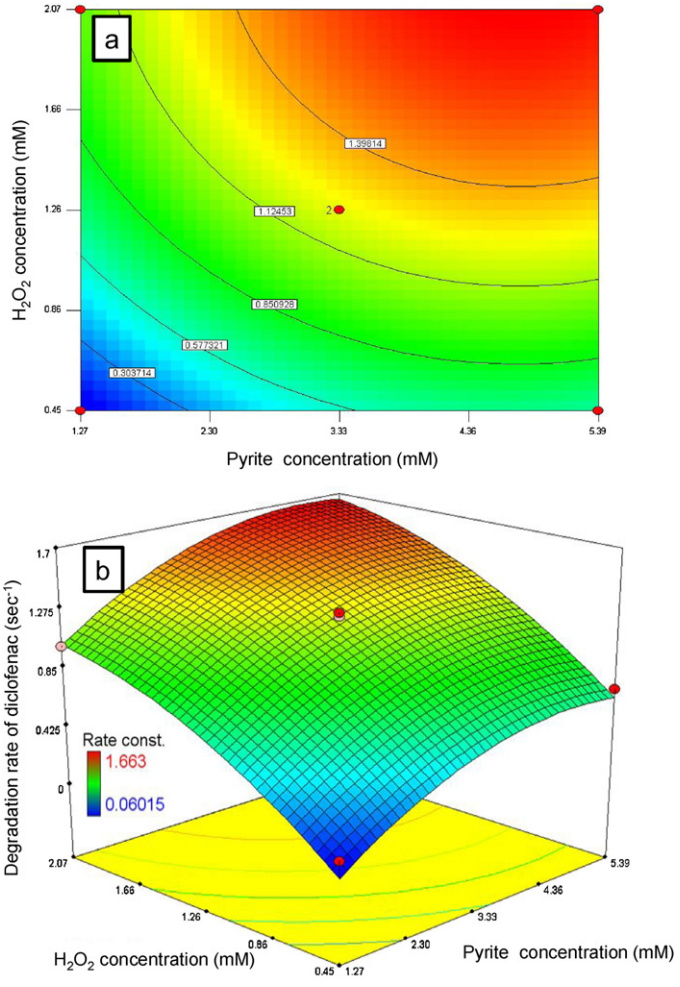


**Fig. 9.** (a) Two-dimensional contour plots and (b) three-dimensional response plots for the degradation rate constants of diclofenac as functions of pyrite and $H_2O_2$ loadings. Experimental boundary conditions: $[Diclofenac]_0 = 0.017$ mM, $[pyrite]_0 = 0.42–6.24$ mM, $[H_2O_2]_0 = 0.12–2.40$ mM, and temperature = 25 ± 0.5 °C.

**Table 2**
Experimental design matrix and results of the degradation of diclofenac by pyrite Fenton system.

| Trial no. | Actual values | | Coded values | | Degradation rate ($s^{-1}$) | |
|---|---|---|---|---|---|---|
| | $X_1$: Pyrite (mM) | $X_2$: $H_2O_2$ (mM) | $X_1$ | $X_2$ | Experimental | Predicted |
| 1 | 6.24 | 1.26 | 2 | 0 | 1.25 | 1.23 |
| 2 | 0.42 | 1.26 | −2 | 0 | 0.28 | 0.35 |
| 3 | 3.33 | 0.12 | 0 | −2 | 0.06 | 0.18 |
| 4 | 5.39 | 0.45 | 1 | −1 | 0.70 | 0.64 |
| 5 | 3.33 | 1.26 | 0 | 0 | 1.22 | 1.23 |
| 6 | 1.27 | 2.07 | −1 | 1 | 1.00 | 1.02 |
| 7 | 3.33 | 2.40 | 0 | 2 | 1.66 | 1.59 |
| 8 | 5.39 | 2.07 | 1 | 1 | 1.58 | 1.65 |
| 9 | 1.27 | 0.45 | −1 | −1 | 0.15 | 0.03 |
| 10 | 3.33 | 1.26 | 0 | 0 | 1.25 | 1.23 |

**Table 3**
Results of ANOVA analysis derived by response surface model.

| Source | Sum of squares | Degree of freedom | Mean square | $F$ value | $p$-value Prob > $F$ | |
|---|---|---|---|---|---|---|
| Model | 3.04 | 5 | 0.61 | 51.81 | 0.0010 | Significant |
| $X_1$: pyrite | 0.77 | 1 | 0.77 | 65.96 | 0.0012 | |
| $X_2$: $H_2O_2$ | 2.00 | 1 | 2.00 | 170.74 | 0.0002 | |
| $X_1X_2$ | 1.600E−4 | 1 | 1.600E−4 | 0.014 | 0.9127 | |
| $X_1^2$ | 0.23 | 1 | 0.23 | 19.43 | 0.0116 | |
| $X_2^2$ | 0.14 | 1 | 0.14 | 11.79 | 0.0265 | |
| Residual | 0.047 | 4 | 0.012 | | | |
| Lack of fit | 0.047 | 3 | 0.016 | 36.87 | 0.1203 | Not significant |
| Pure error | 4.205E−4 | 1 | 4.205E−4 | | | |
| Cor. total | 3.09 | 9 | | | | |

$R^2$ = 0.985, Adjusted $R^2$ = 0.966.

concentration in suspension proportionally increased the aqueous Fe(II) concentration as shown in Fig. 2(b), which leads to the improvement of HO• formation [25] and enhancement of diclofenac degradation in the pyrite Fenton reaction. However, excessive amount of aqueous Fe(II) in pyrite suspension may promote the unwanted consumption of HO• as shown in Eq. (6) which can negatively affect the oxidative degradation of diclofenac by HO•.

As similar to the result of pyrite loading, increase of $H_2O_2$ to the certain level can enhance the oxidative degradation of diclofenac in pyrite Fenton system due to the improvement of HO• formation, while excess amount of $H_2O_2$ in pyrite suspension readily reacts with generated HO• ($k_{HO^\bullet,\ H_2O_2} = 2.1 \times 10^9\ M^{-1}\ s^{-1}$) [47] (Eq. (11)) leading to negative effect on the oxidative degradation of diclofenac by HO•.

$$H_2O_2 + HO^\bullet \rightarrow OOH^\bullet + H_2O \quad (11)$$

However, both self scavenging effects by excessive amounts of pyrite and $H_2O_2$ did not seem to be significant in pyrite Fenton system, which can lead to the rapid deceleration of degradation kinetics of organic contaminants [48–50].

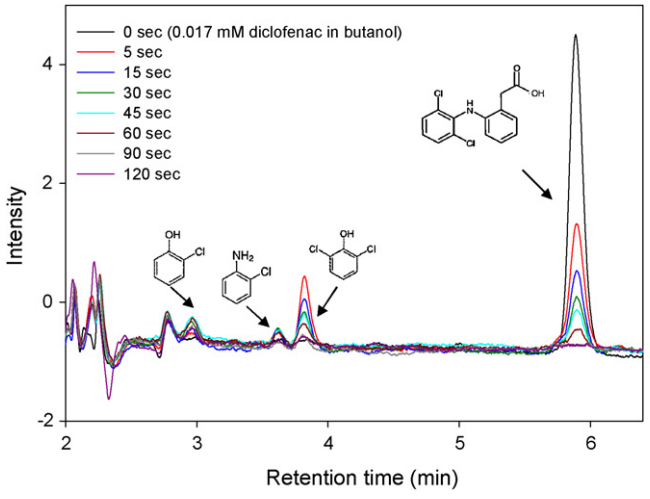


**Fig. 10.** HPLC spectra showing the decrease of diclofenac concentration with formation of products (2,6-dichlorophenol, 2-chloroaniline, and 2-chlorophenol) during the oxidative degradation of diclofenac by pyrite Fenton system. $[Diclofenac]_0$ = 0.017 mM, $[pyrite]_0$ = 0.5 mM, $[H_2O_2]_0$ = 1.0 mM, and temperature = 25 ± 0.5 °C.

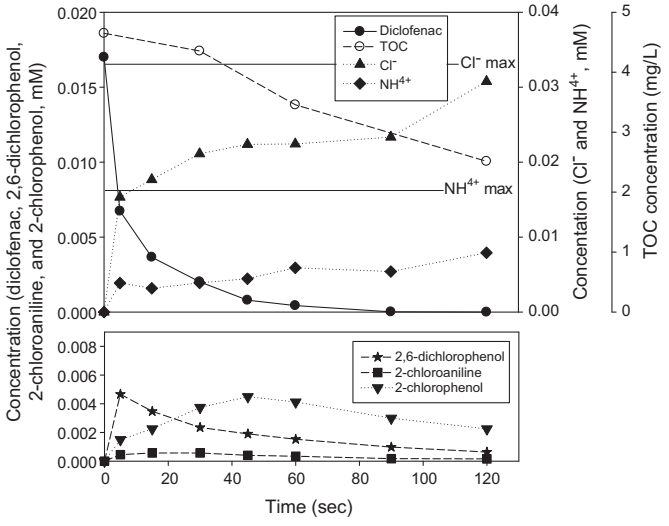


**Fig. 11.** Release of chloride ions ($Cl^-$) and ammonium ($NH^{4+}$) and decrease of TOC, 2,6-dichlorophenol, 2-chloroaniline, and 2-chlorophenol during the oxidative degradation of diclofenac by pyrite Fenton system. $[Diclofenac]_0$ = 0.017 mM, $[pyrite]_0$ = 0.5 mM, $[H_2O_2]_0$ = 1.0 mM, and temperature = 25 ± 0.5 °C.

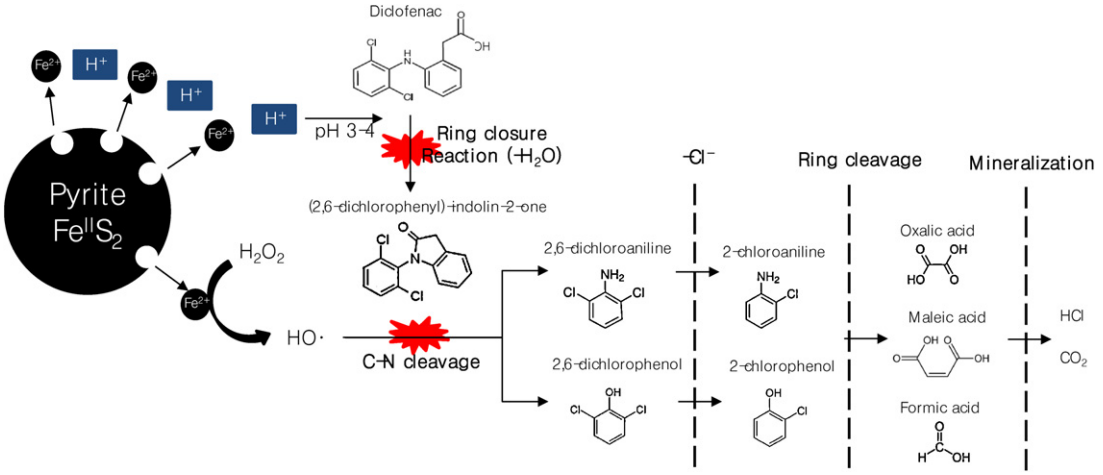


**Fig. 12.** Proposed degradation pathway for oxidative degradation of diclofenac by pyrite Fenton system.

### 3.5. Degradation products of diclofenac

To understand the degradation mechanism of diclofenac through pyrite catalyzed Fenton oxidation, byproducts formed during reaction were analyzed. Fig. 10 shows HPLC chromatogram of diclofenac and other major byproducts. The peak at 5.9 min (diclofenac) completely disappeared in 90 s, while peaks at 3.8 (2,6-dichlorophenol) and 3.6 min (2-chloroaniline) appeared at 5 s and almost disappeared at 120 s. Approximately, 0.0047 mM of 2,6-dichlorophenol was produced at 5 s, then continuously decreased to 0.0006 mM at 120 s, while the highest amount of 2-chloroaniline (0.0006 mM) was observed at 30 s and almost completely degraded at 120 s (Fig. 11). In addition, the peak at 2.95 min (2-chlorophenol) increased until 45 s and decreased as the reaction further proceeded (Fig. 10). The concentration of 2-chlorophenol increased to 0.0046 mM until 45 s and decreased to 0.0022 mM at 120 s (Fig. 11). The intermediates detected in this study indicate that C—N cleavage reaction occurred during the oxidative degradation of diclofenac in pyrite Fenton system (Fig. 12). Prior to C—N cleavage, diclofenac can be dehydrated to form (2,6-diclorophenyl)-indolin-2-one (i.e., ring closure reaction) due to the acidic pH in pyrite suspension [21,51]. Then, (2,6-diclorophenyl)-indolin-2-one may be transformed to 2,6-dichlorophenol and 2,6-dicloroaniline by HO• attack and further dechlorinated to form 2-chlorophenol and 2-chloroaniline in pyrite Fenton system. This indicates that parallel oxidation processes to form 2-chlorophenol and 2-chloroaniline can occur during the degradation of diclofenac by pyrite Fenton system, which is consistent with previously reported data of sonolysis [21]. Phenylacetic acids such as 2-hydroxyphenylacetic acid and 2-aminophenylacetic acid were also detected during the oxidative sonolysis of diclofenac at neutral pH due to an initial attack of HO• [21]. However, we did not observe the phenylacetic acids because acidic suspension pH of pyrite Fenton may lead to formation of (2,6-diclorophenyl)-indolin-2-one at an early stage of degradation before the HO• attack. To investigate the mineralization of diclofenac, concentrations of chloride ions, ammonium, and TOC were measured during the oxidative degradation of diclofenac by pyrite Fenton system (Fig. 11). The concentration of chloride ions significantly increased as pyrite Fenton reaction proceeded, and reached 91% of the initial diclofenac concentration at 120 s. Significant release of chloride ions during the oxidation of diclofenac indicates that 2-chlorophenol and 2-chloroaniline may be further oxidized to oxalic, maleic, and formic acids or completely mineralized to HCl and $CO_2$ [20,21]. The concentration of ammonium also increased as the pyrite Fenton reaction initiated, and reached 47% of the initial diclofenac concentration at 120 s. Approximately, 0.013 mM of ammonium (76% of initial diclofenac) was measured after 300 s reaction (data not shown). At the same time, initial TOC (4.7 mg $L^{-1}$) decreased to 2.5 mg $L^{-1}$ at 120 s (Fig. 11) and further decreased to 0.9 mg $L^{-1}$ at 300 s (data not shown) indicating that 81% of diclofenac was mineralized to HCl or $CO_2$ in the pyrite Fenton system. The significant decrease of dissolved organic carbon was also observed during the degradation of diclofenac by photo-Fenton reaction, resulting in the complete mineralization of diclofenac [20]. These NH-bridge cleavage and TOC removal have been considered as signs of complete mineralization of diclofenac in AOPs [8,20]. The results showed that pyrite can be a promising catalyst to effectively mineralize diclofenac in a relatively short reaction time compared to other AOPs confirming the great advantage of pyrite Fenton system for the oxidative degradation of diclofenac [8,20,21].

## 4. Conclusion

In recent years, iron-bearing soil minerals such as magnetite and feroxyhyte have been used as heterogeneous catalysts to oxidatively degrade various types of organic contaminants (i.e., 2,4-dichlorophenol, polycyclic aromatic hydrocarbons, and methylene blue) [52–54]. We also demonstrated that pyrite catalyzed Fenton reaction can rapidly (within 120 s) and completely degrade diclofenac without formation of toxic products. The pyrite Fenton system provided proper pH condition (pH 3–4) and appropriate amount of aqueous Fe(II) which led to the enhanced oxidation of diclofenac (100%) than that by classic Fenton system (65%). The continuous dissolution of Fe(II) from pyrite surface seems to be a key factor to complete the oxidation of diclofenac by continuously producing the HO• and inhibiting quenching reactions. The major aromatic intermediates such as 2,6-dichlorophenol, 2-chloroaniline, and 2-chlorophenol were also rapidly degraded by the HO• attack and successfully mineralized during the pyrite Fenton reaction. Finally, increase of chloride and ammonium concentrations and decrease of total organic carbon confirmed that diclofenac can be mineralized to HCl and $CO_2$ by the pyrite Fenton system. Therefore, pyrite Fenton system can overcome the limitations of conventional AOPs showed relatively slow and incomplete oxidation of diclofenac with production of toxic products. This system may be easily applied to the STPs for diclofenac removal due to its abundance in our nature and very simple process. The experimental results obtained from this study can provide basic knowledge to understand the oxidative degradation mechanism of diclofenac in the presence of pyrite with $H_2O_2$ and

to design a heterogeneous Fenton system with iron sulfide mineral for treatment of water contaminated with various NSAIDs in STPs.

## Acknowledgments

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